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On the Systems: Barium Oxide—Acetic Acid—Water and Magnesium Oxide—Acetic Acid—Water.

By

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The equilibrium of the systems consisting of barium or magnesium oxide, acetic acid and water at 25·0°C. has been studied; and the present article is an account of the results.

I. The System: Barium Oxide, Acetic Acid and Water.

The materials used were barium hydroxide, barium acetate, acetic acid and water. They were mixed in different proportions, the free base and acid not being used at the same time; and each mixture was put in an Erlenmeyer flask of a capacity of about 50 cc. The flasks were made to rotate in a thermostat at 25·0° for at least one day; then the solution was separated from the residue, and both, the latter still wet with the former, were analysed for barium and acetic acid.

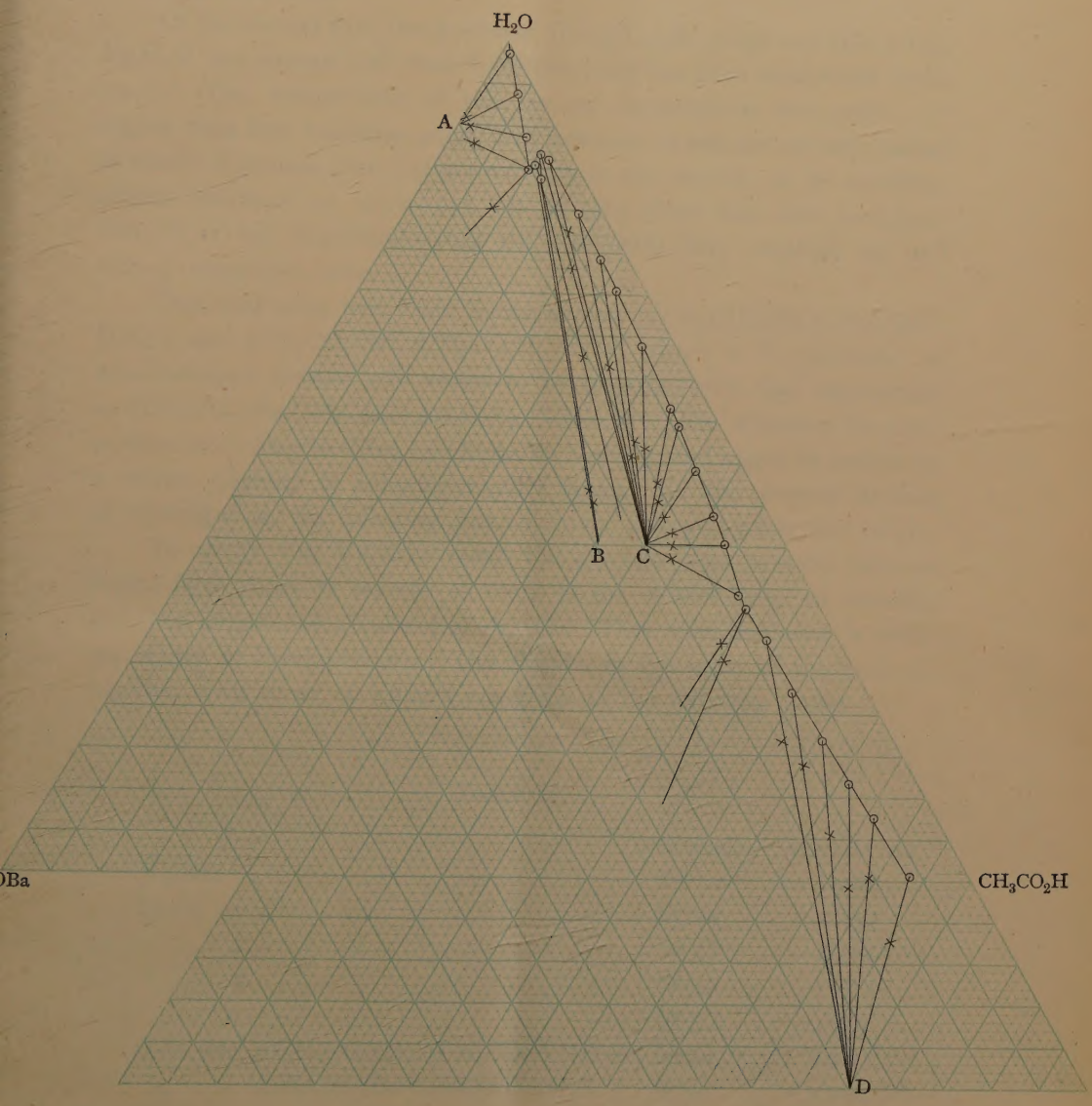
The analysis was carried out in the following way. A given quantity of a sample, mixed with some water and phosphoric acid, was subjected to distillation; and when the liquid in the distillation flask was reduced to a small quantity, the distillation was continued by passing steam through, until the distillate ceased to react acid to a litmus paper. Of this distillate, acetic acid was titrated with a decinormal solution of sodium hydroxide, using phenolphthalein as indicator. Barium was determined as the sulphate in the residue in the distillation flask in the usual way. The amount of water was found by noting the difference.

The results are given in Table 1 and graphically represented in Fig. 1.

TABLE I.

No.	Solution.			Residue, wet with the solution.			Residue.
	OBa	CH_3CO_2H	H_2O	OBa	CH_3CO_2H	H_2O	
1	0·39	0	99·61	—	—	—	$(HO)_2Ba.8H_2O$.
2	1·06	0·56	98·31	9·10	0·26	90·63	„
3	2·30	4·06	93·64	8·25	1·04	90·72	„
4	4·06	7·49	88·45	9·22	1·09	89·71	„
5	5·22	9·80	84·94	9·82	2·73	87·71	$(HO)_2Ba.8H_2O$; $(CH_3CO_2)_2Ba.3H_2O$.
6	5·24	9·87	84·89	11·36	8·64	80·00	$(CH_3CO_2)_2Ba.3H_2O$.
7	4·92	10·04	85·06	17·76	35·91	46·31	„
8	5·10	11·53	83·37	18·00	37·00	45·02	$(CH_3CO_2)_2Ba.3H_2O$; $3(CH_3CO_2)_2Ba;3CH_3CO_2H.11H_2O$.
9	5·05	11·49	83·52	10·76	26·85	62·38	$3(CH_3CO_2)_2Ba.3CH_3CO_2H.11H_2O$.
10	3·88	10·09	86·30	6·86	20·21	72·98	„
11	2·95	11·35	85·72	5·10	17·37	77·52	„
12	2·94	17·58	79·49	8·51	30·21	61·32	„
13	3·21	22·76	74·03	9·30	34·30	56·37	„
14	3·44	26·21	70·36	10·34	37·32	52·35	„
15	3·91	32·17	63·92	9·80	38·91	51·29	„
16	4·53	9·04	56·44	10·25	42·52	47·23	„
17	4·89	41·07	54·05	11·37	43·64	44·98	„
18	5·62	45·53	48·84	11·82	45·08	43·10	„
19	6·29	50·03	43·63	11·78	47·09	41·15	„
20	6·80	53·15	40·05	12·28	47·87	39·84	„
21	8·10	57·80	36·09	12·97	48·53	38·50	„
22	8·23	59·13	32·63	12·80	59·00	28·20	$3(CH_3CO_2)_2Ba.3CH_3CO_2H.11H_2O$; $(CH_3CO_2)_2Ba.2CH_3CO_2H$.
23	8·22	59·41	32·36	13·53	60·12	26·35	$(CH_3CO_2)_2Ba.2CH_3CO_2H$.
24	7·94	63·77	28·31	12·06	71·58	16·36	„
25	8·02	69·71	22·27	11·14	75·54	13·32	„
26	7·88	75·70	16·43	12·72	82·12	5·16	„
27	7·62	81·16	11·24	13·69	87·66	−1·33	„
28	7·23	85·96	6·82	11·09	88·90	0	„
29	6·85	93·11	0·03	12·28	95·15	−7·43	„

Fig. 1.



A. $(HO)_2$ Ba. $8H_2O$.

B. $(CH_3CO_2)_2$ Ba. $3H_2O$.

C. $3(CH_3CO_2)_2$ Ba. $3CH_3CO_2H$. $11H_2O$.

D. $(CH_3CO_2)_2$ Ba. $2CH_3CO_2H$.

In Fig. 1, triangular coordinates are used, barium oxide, acetic acid and water, as the components, being represented by the angular points. The compositions of the residues were estimated in the usual way, as seen from the figure, and are given in formulas in the last column of the table.

Of the normal salt, two hydrates, $(CH_3CO_2)_2Ba.3H_2O$ and $(CH_3CO_2)_2Ba.H_2O$, are known and their transition point has been determined to be 24·7°.[1] The temperature of the present investigation was only 0·3° higher than that transition point, and moreover it was not an easy matter to obtain a system with the normal salt as the residue, as its solubility attains maximum at about 25°. If we take these facts into consideration, it is not improbable that the trihydrate here obtained at 25° was a metastable state.

Two acid salts have been found, namely $3(CH_3CO_2)_2Ba.3CH_3CO_2H.IIH_2O$ and $(CH_3CO_2)_2Ba.2CH_3CO_2H$. The former is in prismatic or needle-shaped crystals and seems to be identical with that represented as $(CH_3CO_2)_2Ba.CH_3CO_2H.4H_2O$ by Villiers.[2] The difference in composition according to these two formulas is slight, and might be caused by a minute quantity of adhering mother liquor. In the present method of investigation, the adhering mother liquor does not affect the result.

To verify the Villiers's result the crystals were pressed between folded filter paper to remove as much of the mother liquor as possible, and then exposed to a current of dry air. They were analysed in different stages of the procedure. The results, in the order of the analysis, together with those of Villiers are given in the following table.

TABLE II.

	Bariumacetate	Excessive acid
Villiers	65·53	15·85
Iwaki 1.	65·54	16·39
2.	66·28	16·14
3.	66·42	15·79
4.	68·32	15·37
Calc. for $3(CH_3CO_2)_2Ba.3CH_3CO_2H.IIH_2O$	66·94	15·73
,, ,, $(CH_3CO_2)_2Ba.CH_3CO_2H.4H_2O$	65·91	15·49

1 Walker and Fyffe, J. chem. Soc., **83**, 173 (1903).

2 C. R., **85**, 1235 (1877).

As may be seen from the table, it is quite difficult or almost impossible to determine the composition of the crystals by obtaining them pure enough for analysis in the usual way.

To make sure, another method of analysis was adopted. The mother liquor and the wet residue were diluted or dissolved respectively to a given volume; and an aliquot part was titrated for the free acid, while in another portion barium was determined. From this data the percentage composition of the sample was calculated, and the results are given in the following table.

TABLE III.

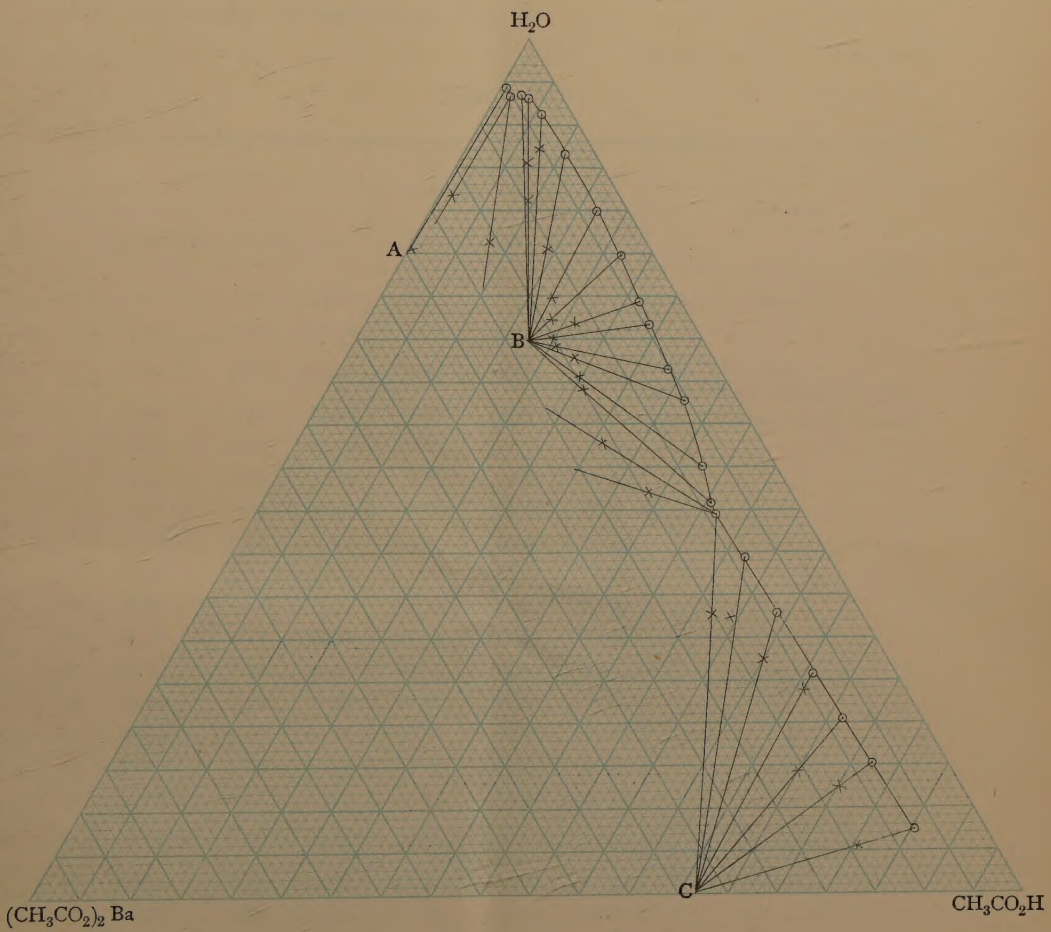
No.	Solution.			Residue, wet with the solution.			Residue.
	CH_3CO_2H	$(CH_3CO_2)_2Ba$	H_2O	CH_3CO_2H	$(CH_3CO_2)_2Ba$	H_2O	
1	3·30	3·48	93·22	9·81	9·85	80·35	$3(CH_3CO_2)_2Ba.3CH_3CO_2H.IIH_2O$.
2	10·23	3·14	86·64	14·04	10·40	75·56	„
3	16·92	3·24	79·84	17·46	12·77	69·68	„
4	20·60	3·62	75·77	18·77	14·19	67·04	„
5	26·48	4·41	69·10	21·04	12·11	66·86	„
6	28·72	4·52	66·77	19·87	15·12	64·95	„
7	33·14	5·23	61·62	20·67	15·30	64·04	„
8	36·54	5·60	57·86	23·18	14·00	62·82	„
9	42·08	7·85	50·05	24·87	14·52	60·60	„
10	45·28	8·82	45·93	25·95	14·90	59·14	„
11	46·90	8·92	44·17	23·54	15·92	60·57	„

From this data is derived the same conclusion as before as to the composition of the residue, as seen in Fig. 2; and Villiers's formula is very improbable.

Villiers[1] obtained another acid salt from a glacial acetic acid solution of barium acetate. It was so unstable that its formula could not be determined definitely; but he suggested from anaytical results, that it might have the formula $(CH_3CO_2)_2Ba.2CH_3CO_2H.2H_2O$. In the present investigation, the crystals obtained from solutions, comparatively concentrated for acetic acid, were silky, as those described by Villiers, and had the composition, $(CH_3CO_2)_2Ba.2CH_3CO_2H$, as graphically estimated in Fig. 1.

1 *Loc. cit.*

Fig. 2.



A. (CH_3CO_2) Ba. $3H_2O$.

B. $3(CH_3CO_2)_2$ Ba. $3CH_3CO_2H$. $11H_2O$.

C. $(CH_3CO_2)_2$ Ba. $2CH_3CO_2H$.

Experiments were begun for the study of the normal, acid and basic acetates of barium, and barium oxide, acetic acid and water were considered to be the components as in Table I and Fig. 1. The non-existence of any basic salt being ascertained, it became convenient to take acetic acid, barium acetate and water as the components; and to make the equilibrium state more intelligible, the following table was derived from the foregoing, supplemented by some new experiments. It is graphicplly represented in Fig. 2.

TABLE IV.

No.	Solution.			Residue, wet with the solution			Residue.
	CH_3CO_2H	$(CH_3CO_2)_2Ba$	H_2O	CH_3CO_2H	$(CH_3CO_2)_2Ba$	H_2O	
1	0	5·18	94·80	—	—	—	$(CH_3CO_2)_2Ba.3H_2O$.
2	0·41	5·21	94·36	0·30	24·11	75·59	,,
3	1·40	5·34	93·22	1·22	21·94	76·84	$(CH_3CO_2)Ba.3H_2O$; $3(CH_3CO_2)_2Ba.3CH_3CO_2H.11H_2O$.
4	1·46	5·32	63·22	7·87	15·89	76·23	$3(CH_3CO_2)_2Ba.3CH_3CO_2H.11H_2O$.
5	2·42	4.03	93·56	6·96	7·36	85·69	,,
6	3·30	3·48	93·22	9·81	9·85	80·35	,,
7	5·61	3·04	91·35	7·56	5·38	87·12	,,
8	10·23	3·14	86·64	14·04	10·40	75·56	,,
9	16·92	3·24	79·84	17·46	12·77	69·68	,,
10	20·60	3·62	75·77	18·77	14·19	67·04	,,
11	26·48	4·41	69·10	21·04	12·11	66·86	,,
12	28·72	4·52	66·77	19·87	15·12	64·95	,,
13	33·14	5·23	61·62	20·67	15·30	64·04	,,
14	36·54	5.60	57·86	23·18	14·00	62·82	,,
15	42.08	7·85	50·05	24·87	14·52	60·60	,,
16	45·28	8·82	45·93	25·95	14·90	59·14	,,
17	46·51	8·87	44·61	30·85	16·19	52·93	$3(CH_3CO_2)Ba.3CH_3CO_2H.11H_2O$; $(CH_3CO_2)_2Ba.2CH_3CO_2H$
18	46·50	8·97	44·52	38·30	14·68	47·02	$(CH_3CO_2)_2Ba.2CH_3CO_2H$
19	46·49	9·10	44·40	51·78	15·49	32·71	,,
20	51·98	8·62	39·37	53·96	13·71	32·32	,,
21	58·35	8·72	32·93	59·94	12·54	27·53	,,
22	65·77	8·40	25·80	65·66	10·31	24·02	,,
23	71·34	8·25	20·41	69·83	15·85	14·32	,,
24	77·06	7·79	15·14	75·06	12·47	12·47	,,
25	85·27	7·36	7·39	90·46	14·00	5·53	,,

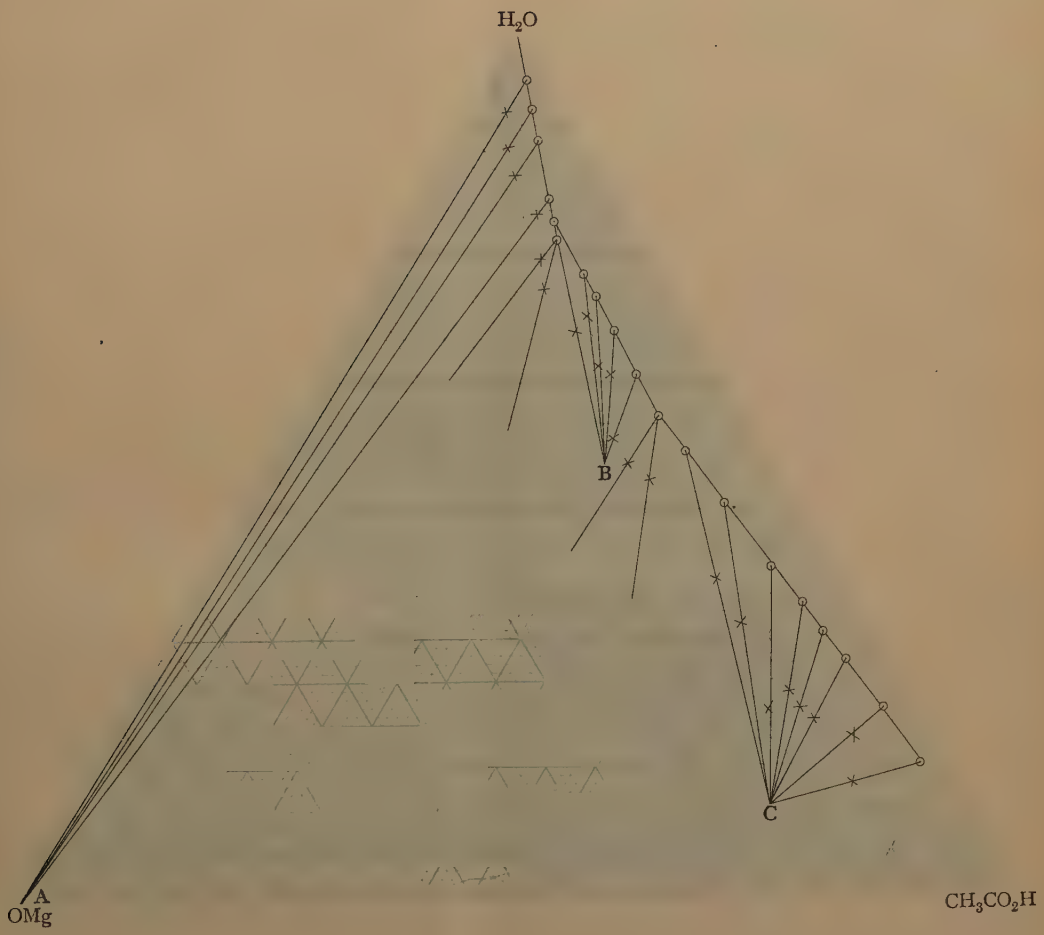
II. The System: Magnesium Oxide, Acetic Acid and Water.

The materials used were magnesium oxide (magnesia usta), acetic acid and water, in some cases magnesium acetate instead of magnesium oxide was used. The experiments were carried out as in the case of barium, except that the rotation in the thermostat was continued for at least two days instead of one. The solution was freed from the residue by a centrifugal filter apparatus. Acetic acid was determined by distillation in the same way as before, and magnesium as the pyrophosphate in the usual way. The results are given in Table 5.

TABLE V.

No.	Solution.			Residue, wet with the solution.			Residue.
	CH_3CO_2H	OMg	H_2O	CH_3CO_2H	OMg	H_2O	
1	3·36	1·73	94·91	3·32	5·53	91·14	OMg
2	5·65	2·93	91·41	5·35	7·66	86·99	„
3	8·06	4·21	87·73	7·80	8·43	83·77	„
4	12·46	6·54	80·99	12·23	8·50	79·27	„
5	15·46	8·24	76·30	15·09	10·92	73·99	$\left\{\begin{matrix}\text{OMg};\\(CH_3CO_2)_2Mg.4H_2O,\end{matrix}\right.$
6	15·38	8·31	76·30	17·29	12·20	70·49	$(CH_3CO_2)_2Mg.4H_2O.$
7	14·25	7·24	78·51	22·85	11·76	65·39	„
8	20·19	7·47	72·32	23·14	9·63	67·22	„
9	22·93	7·60	69·47	26·93	11·37	61·69	„
10	26·61	7·74	65·65	28·69	10·71	60·61	„
11	31·37	7·99	60·64	32·51	14·20	53·29	„
12	36·23	8·18	55·59	35·80	14·06	50·13	$\left\{\begin{matrix}(CH_3CO_2)_2Mg.4H_2O;\\2(CH_3CO_2)_2Mg,3CH_3CO_2H.3H_2O.\end{matrix}\right.$
13	35·77	8·17	56·06	38·93	12·88	48·18	$2(CH_3CO_2)_2Mg.3CH_3CO^2H.3H_2O.$
14	40·87	7·42	51·71	51·31	11·95	36·74	„
15	47·86	6·74	45·39	56·30	12·00	31·71	„
16	56·16	5·81	38·04	64·28	14·21	21·53	„
17	61·59	4·68	33·75	65·25	11.13	23·64	„
18	65·19	4·36	30·46	67·41	11·11	21·48	„
19	69·13	3·75	27·11	69·26	10·60	20·15	„
20	75·93	2·85	21·21	74·64	7·32	18·02	„
21	82·90	2·23	14·87	77·14	10·04	12·81	„

Fig. 3.

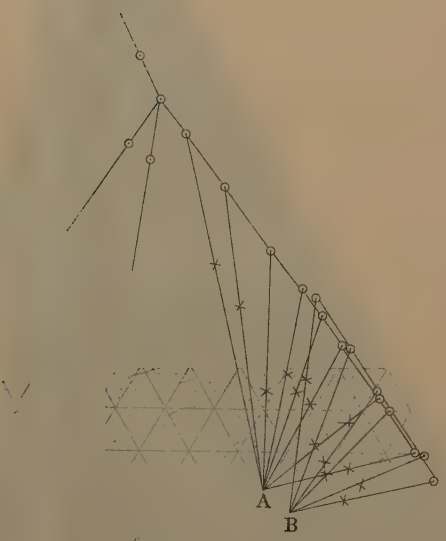


A. OMg.

B. $(CH_3CO_2)_2$ Mg. $4H_2O$.

C. $2(CH_3CO_2)_2$ Mg. CH_3CO_2H. $3H_2O$.

Fig. 4.



CH_3CO_2H

A. $2(CH_3CO_2)_2$ Mg. $3CH_3CO_2H$. $3H_2O$.

B. $5(CH_3CO_2)_2$ Mg. $10CH_3CO_2H$. $7H_2O$.

The data in Table 5 are graphically represented in Fig. 3, referring to triangular coordinates; and the chemical formulas of the residues, estimated from the figure in the usual way, are given in the last column of the table.

The normal salt with four molecules of water of crystallization is one well known in the literature of the subject.

No acid salt has yet been described in the literature. When magnesium acetate was dissolved in hot acetic acid and shaken in a thermostat at 25·0° for several days, an acid salt crystallised out. Again, magnesium oxide was dissolved in glacial acetic acid, the solution was evaporated to a certain extent; and when the cooled solution was rubbed by a glass rod against the side of the vessel, the syrupy solution solidified to a mass, due to the formation of an acid salt. Thus having obtained some evidence of the existence of an acid salt, a systematic study for it was undertaken; and the results are to be found in Table 5. The composition of the acid salt was estimated graphically to be $2(CH_3CO_2)_2Mg.3CH_3CO_2H.3H_2O$. It is a precipitate of microscopic rhombic plates.

When the experiments were nearly closed, another kind of acid salt was found from a solution in concentrated acetic acid. The crystalline form was almost like that of the other. The experimental data for that acid salt are given in Table 6.

TABLE 6.

No	Solution.			Residue, wet with the solution.			Residue.
	CH_3CO_2H	OMg	H_2O	CH_3CO_2H	OMg	H_2O	
1	63·50	3·91	32·59	67·38	9·49	23·12	$5(CH_3CO_2)_2Mg.10CH_3CO_2H.7H_2O$
2	70·09	3·17	26·73	72·23	12·19	15·59	,,
3	75·39	2·87	21·73	74·32	12·31	13·39	,,
4	77·84	2·83	19·33	74·91	12·66	12·45	,,
5	84·05	1·61	14·35	79·53	9·77	10·65	,,
6	86·50	2·19	11·31	78·72	12·46	8·82	,,

These data together with those in Table 5 relating to the acid salt are graphically represented in Fig. 4. The new data led to the formula $5(CH_3CO_2)_2Mg.10CH_3CO_2H.7H_2O$. This was almost always produced from solutions in concentrated acetic acid and the other from such

solutions only when induced by the presence of the same kind of crystals. These facts, together with the relative position of the solubility curves, seem to evidence that the heptahydrated acid salt is a stable one at least in concentrated acetic acid solutions; but time did not allow further study of the acid salts.

Lastly, as to the basic salt; the problem has been studied by Kubel.[1] From very slight differences in the density of solutions differently treated, he concluded that there exits an insoluble basic salt. His method of investigation and his conclusion, however, seem to me not free from objections.

In the present investigation the existence of the basic salt was sought by adding acetic acid in different proportions to mixtures of magnesium oxide and water. The mixtures were boiled for ten minutes and then rotated in a thermostat for more than two days. The solutions being syrupy, the separation of the residue from the mother liquor was very difficult; and, since the solution and the wet residue were very like in composition, it was almost impossible to estimate graphically the composition of the residue. But the residue was only the oxide, and there was no sign of the existrence of any basic salt in a solid state.

Summary.

1. The equilibrium of the systems: barium oxide, acetic acid and water, and magnesium oxide (magnesia usta), acetic acid and water, has been studied at 25·0°.

2. The following acid salts, hitherto unknown, have been found:

a. $3(CH_3CO_2)_2Ba.3CH_3CO_2H.11H_2O$,
b. $(CH_3CO_2)_2Ba.2CH_3CO_2H$,
c. $2(CH_3CO_2)_2Mg.3CH_3CO_2H.3H_2O$,
d. $5(CH_3CO_2)_2Mg.10CH_3CO_2H.7H_2O$.

3. The acid salts described by Villiers, as having the composition respectively of $(CH_3CO_2)_2Ba.CH_3CO_2H.4H_2O$ and $(CH_3CO_2)_2Ba.2CH_3CO_2H.2H_2O$(?), seem to be nothing others than those here given.

4. No basic salt in a solid state exists in either case.

To Prof. Y. Osaka, at whose suggestions this work was undertaken, the auther wishes to express thanks for his interest and encouragement.

[1] Arch. Pharm. [3] **230**, 173 (1892.)

A New Method for the Determination of Sodium and Potassium in a Mixture of their Salts.

By

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(Received October 10, 1914.)

For the determination of potassium in the presence of sodium, precipitation as potassium chloroplatinate is a most accurate and moreover very convenient method, but the high price of platinum is a disadvantage. Indirect analysis, depending on the difference of the atomic weights of these two elements is often employed, but from it in general great accuracy can not be expected. At the suggestion of Prof. Y. Osaka the writer has undertaken to work out a new analytical method for the determination of sodium and patassium, each in the presence of the other, utilizing the slight solubility of potassium hydrogen tartrate.

When a given quantity of a mixture of sodium and potassium salts is mixed with a given quantity of sodium hydrogen tartrate in solution, and the temperature and the total volume of the solution is kept constant, the concentration of the tartrates remaining in the solution is a function of the percentage of potassium in the sample. If this function be given in the form of a curve, a mixture of sodium and potassium salts may be analysed by determining the concentration of the tartrates remaining in the solution. Naturally any other quantity which is a function of the concentration of the tartrates may be taken instead in drawing such a curve. Such curves have been sought for mixtures of chlorides and of sulphates, as they are the most common cases.

1. *Sodium and Potassium Chlorides.*

The sodium and potassium chlorides used were the purest preparations of C. Merck and sodium hydrogen tartrate used was an ordinary salt recrystallised. A standard solution of sodium hydroxide was pre-

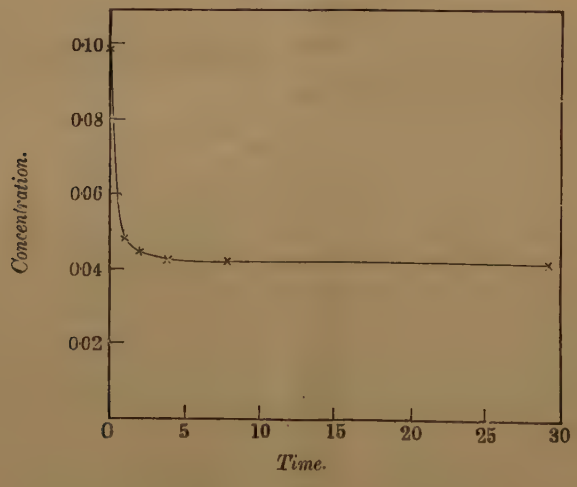
pared from metallic sodium and water free from carbonic acid and standardised by succinic acid.

To find the time necessary for the reaction in question to attain a state of equilibrium, 0·4980 grams of potassium chloride and 1·0456 grams sodium hydrogen tartrate were dissolved to an aqueous solution of 70 c.c. at 25·0° C. This was shaken constantly in a well stoppered flask in a thermostat of the same temperature; 10 c.c. of the solution were taken out at certain intervals of time; and the concentration of the tartrates determined by a method to be described later. The results were as follows:

TABLE I.

Time in hours.	Concentration of the tartrates in solution in mols per liter.
0	0·0993
1	0·0481
2	0·0447
3¾	0·0425
7¾	0·0422
29¼	0·0415

This is graphically represented in Fig. 1; and it may be concluded that equilibrium was attained practically in five hours.



The Determination of the Standard Curve.

1·000 gram of mixed chlorides of known composition and 2·400 grams of sodium hydrogen tartrate were dissolved in water and diluted

to 50 c.c. at 25·0°. It was shaken in a thermostat at the same temperature for at least five hours, and then allowed to stand in the same thermostat. When the precipitate subsided, 20 c.c. of the clear solution were taken out, evaporated to dryness; and the residue brought to red heat, when it partially fused. The alkalies thus produced were extracted with a given amount of a standard solution of hydrochloric acid, the excess of the acid being back-titrated with a standard solution of sodium hydroxide, using methyl orange as indicator. The results are given in the following table:—

TABLE II.

Mixed chlorides taken. Molar percentages.		Mixed chlorides taken. Grams.		Normal hydrochloric acid used. c.c.		
KCl	NaCl	KCl	NaCl	I	II	Mean.
—	100	——	1·0000	5·62	5·59	6·15
2	98	0·0254	0·9742	5·60	5·58	5·60
5	95	0·0629	0·9371	5·54	5·56	5·55
10	90	0·1242	0·8758	5·20	5·23	5·22
20	80	0·2417	0·7582	4·55	4·57	4·56
30	70	0·3534	0·6466	4·02	4·01	4·02
40	60	0·4594	0·5405	3·54	3·54	3·54
50	50	0·5605	0·4395	3·05	3·02	3·04
60	40	0·6567	0·3433	2·56	2·56	2·56
70	30	0·7485	0·2515	2·19	2·17	2·18
80	20	0·8361	0·1639	1·79	1·79	1·79
90	10	0·9199	0·0801	1·47	1·45	1·46
100	—	1·0000	——	1·20	1·19	1·20

As the quantity of hydrochloric acid used is equivalent to that of the tartrates in the original solution it is a function of the amount of sodium and potassium in the sample taken, and is graphically represented in Fig. 2. The quantity of hydrochloric acid solution used is plotted along the axis of ordinate; and in curve I. the percentage by weight of sodium chloride and in curve II. its percentage by mols along the axis of abcissa. As may be seen from the curves, they can not be used for a mixture in which the potassium chloride is less than five percent with the same accuracy as in other cases.

2. *Sodium and Potassium Sulphates.*

The potassium sulphate used was the purest preparation of C. Merck, sodium sulphate was an ordinary salt recrystallised and dehydrated in an air bath at 120°C. The other reagents used were the same as in the case of the chlorides. The period of time required for the attainment of equilibrium was experimentally determined in this case also; and the result was quite the same as in the case of the chlorides.

Thus the deta for the standard curves were obtained by experiments which were carried out quite similarly to those in the case of the chlorides, the only difference being that 2·000 grams of sodium hydrogen tartrate were used instead of 2·400 grams. The results were as follows:

TABLE III.

Mixed sulphates taken. Molar percentages.		Gram.		Normal hydrochloric acid used. c.c.		
K_2SO_4	Na_2SO_4	K_2SO_4	Na_2SO_4	I	II	Mean
—	100	——	1·0000	4·86	4·85	4·86
10	90	0·1199	0·8801	4·44	4·46	4·45
20	80	0·2347	0·7653	3·97	3·99	3·98
30	70	0·3446	0·6554	3·54	3·54	3·54
40	60	0·4499	0·5501	3·11	3·11	3·11
50	50	0·5505	0·4491	2·70	2·70	2·70
60	40	0·6479	0·3521	2·32	2·29	2·31
70	30	0·7411	0·2589	1·94	1·93	1·94
80	20	0·8309	0·1693	1·65	1·66	1·66
90	10	0·9169	0·0831	1·39	1·38	1·39
100	—	1·0000	——	1·17	1·18	1·18

This is graphically represented in Fig. 3 and the curves have the same meaning as in Fig. 2.

3. *Practical Applications.*

To see how far this method of analysis might be relied upon in practice, the following experiments were conducted. 1·000 grams of mixed chlorides or sulphates of known proportions and 2·400 or 2·000 grams of sodium hydrogen tartrate respectively were taken, and treated

Fig. 2.

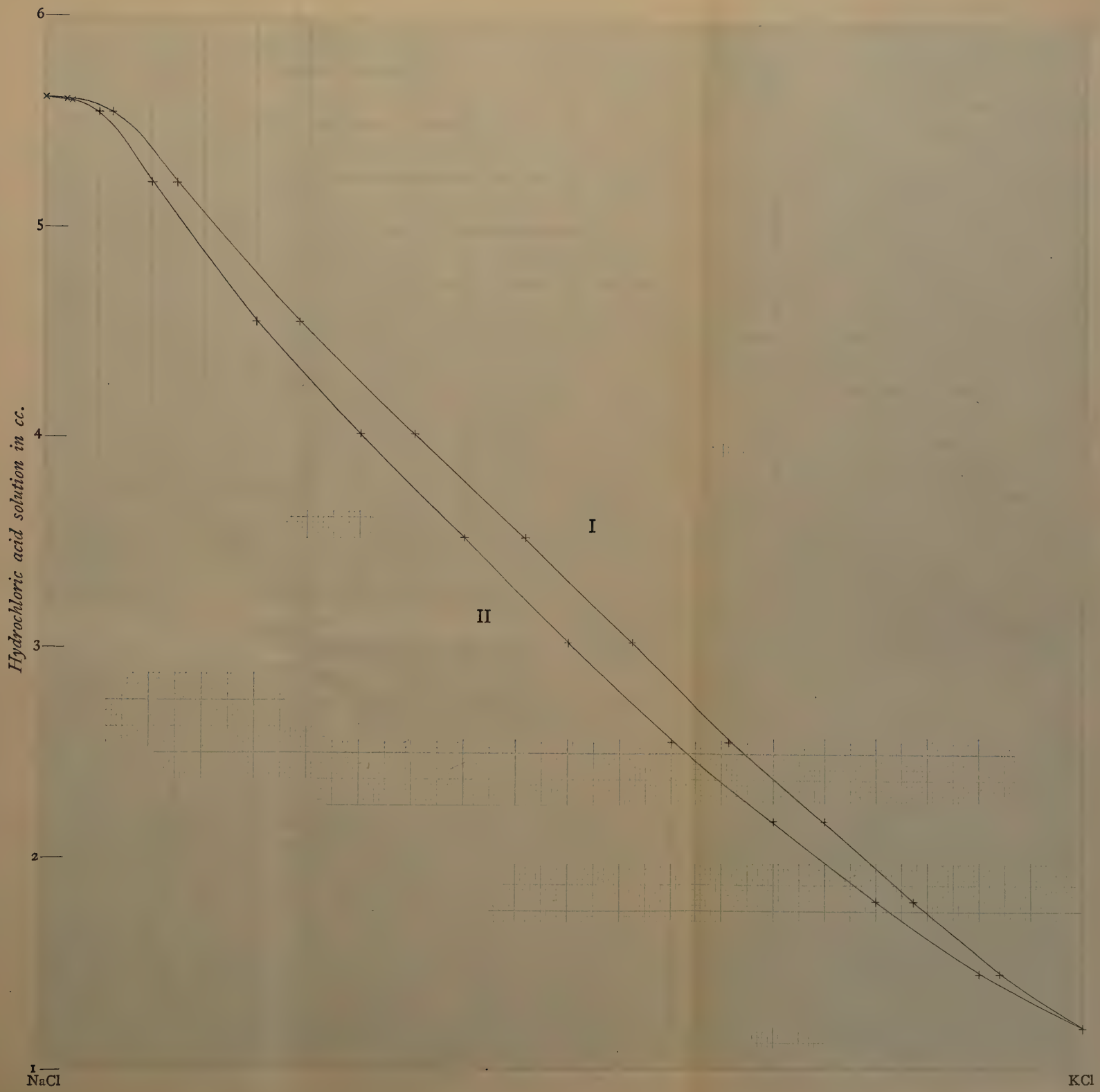
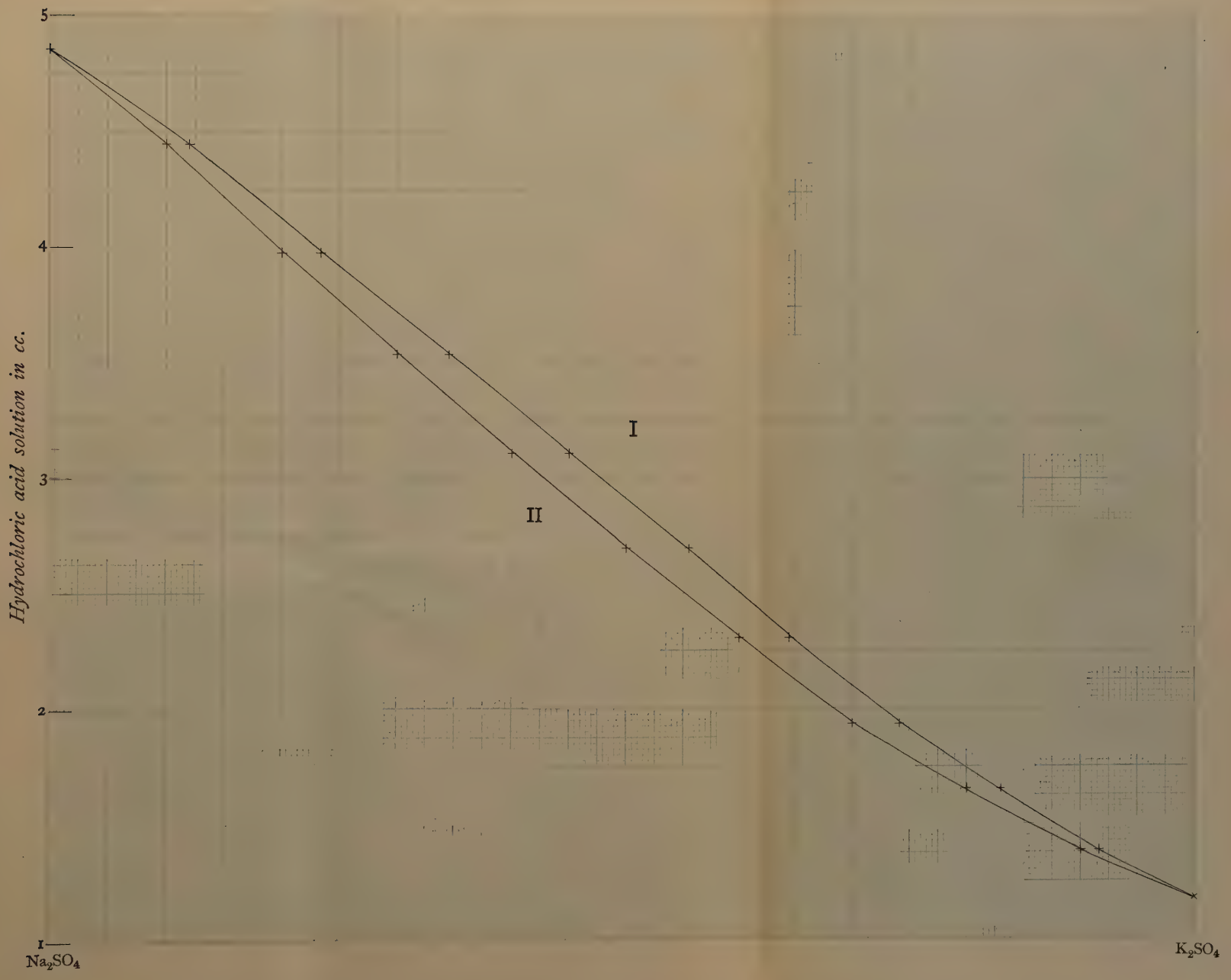


Fig. 3.



as when the data for the fundamental curves were sought. The results were as follows:—

TABLE IV.

Normal hydrochloric acid, required in c.c.	Potassium chloride in the mixture in molar percentage.		
	From the curve.	Taken.	Difference.
5·53	6·6	5·8	0·8
5·45	8·3	8·0	0·3
4·14	33·0	33·2	0·2
3·85	39·5	40·5	1·0
3·22	52·3	52·3	0·0
3·21	52·3	52·4	0·1

TABLE V.

Normal hydrochloric acid, required in c.c.	Potassium sulphate in the mixture in molar percentage.		
	From the curve.	Taken.	Difference.
4·77	2·7	2·8	0·1
3·90	25·5	25·9	0·4
3·19	42·9	43·2	0·3
2·88	50·6	50·6	0·0
1·77	79·2	79·3	0·1
1·59	85·3	84·9	0·4
1·43	90·7	91·1	0·4

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In conclusion I wish to express my sincere thanks to Prof. Y. Osaka for his valuable suggestions and kind instruction during this work.

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On the Double Salt of Sodium and Potassium Sulphates.

By

Kichiro Okada.

(Received October 10, 1914.)

Mixed sulphates of sodium and potassium occur as a mineral glaserite at Stassfurt in Germany. As to its composition and constitution there have been controversies; and a complete literature is to be found in an article by Retgers.[1] According to him, there is only one double salt of the sulphates of the formula, $K_3Na(SO_4)_2$, while Brandrowsky[2] has come to the conclusion that only one double salt of the composition, $2K_2SO_4.Na_2SO_4$, is formed from the solutions in which sodium and potassium salts are present in a molar proportion of 1 : 2 to 1 : 1; and has considered the double salt of Retgers to be nothing but a mixture of this double salt and patassium sulphate. The conclusion of Brandrowsky has been corroborated by Kubierschky,[3] and that of Retgers by Grossner.[4] van't Hoff and Barschall[5] have insisted in their view that glaserite is an extreme end of a long series of solid solutions, saturated with potassium sulphate, having the composition $K_3Na(SO_4)_2$.

Lastly Nacken[6] has corroborated the existence of the double salt $K_3Na(SO_4)_2$, and found that the double salt dissolved sodium sulphate to a certain extent, the solubility increasing with temperature.

At the suggestion of Prof. Y. Osaka the writer has undertaken, from the stand-point of the phase rule, to determine the composition of the double salt, its relation to the solid solutions, and the temperature influence on the solid solutions, utilising the analytical method worked out in the preceeding article.

1 Zs. physik Chem., **6**, 205. (1890).
2 *Ibid.*, **17**, 240 (1895).
3 Berliner SitzBer., (1902), 404.
4 Zs. Kristallogr., **39**, 155 (1904).
5 Berliner SitzBer., (1903), 359; and Zs. physik. Chem., **56**, 212 (1906).
6 Berliner SitzBer., (1910), 1016.

Experiment.

About 10 grams of mixtures of sodium and potassium sulphates of various proportions were dissolved in 10 c.c. of water in a flask of a capacity of about 30 c.c., which was made to rotate in a thermostat for a period of 24 hours or more. The saturated solution was separated from the residue by an apparatus shown in Fig. 1. A is a so-called calsium chloride tube containing purified cotton, and B a receiver, communicating by a long side tube C with a pump. The apparatus was immersed in the thermostat to keep the solution at a constant temperature. After separating the mother liquor from the residue as much as possible by the action of the pump, the latter was pressed between filter paper and dried in an air bath. The solution was evaporated on a water bath to complete dryness. The samples thus obtained were analysed exactly as described in the preceeding article. The results were as follows:

Fig. 1.

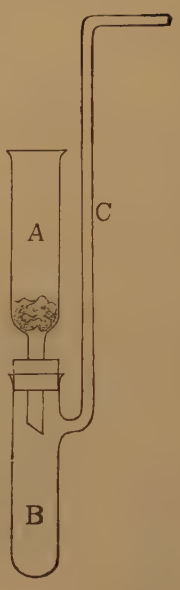


TABLE I.

Temperature: 15·0°.

No.	Sulphates in solution, in molar percentages.		Sulphates in residue, in molar percentages.	
	K_2SO_4	Na_2SO_4	K_2SO_4	Na_2SO_4
1	33·1	66·9	7·3	92·7
2	33·3	66·7	36·2	63·8
3	33·8	66·2	47·4	52·6
4	34·1	65·9	67·5	32·5
5	34·2	65·8	73·0	27·0
6	41·2	58·8	73·1	26·9
7	43·7	56·3	73·2	26·8
8	49·8	50·2	73·6	26·4
9	55·4	44·6	74·6	25·4
10	55·7	44·3	75·0	25·0
11	58·6	41·4	75·3	24·7
12	59·8	40·2	81·8	18·2
13	59·8	40·2	93·8	6·2

Table II.

Temperature: 25·0°

No.	Sulphates in solution, in molar percentages. K_2SO_4	Na_2SO_4	Sulphates in residue, in molar percentages. K_2SO_4	Na_2SO_4
1	19·8	80·2	5·8	94·2
2	20·1	79·9	19·3	80·8
3	19·7	80·3	21·2	78·8
4	20·2	79·3	55·9	44·1
5	20·6	79·4	70·0	30·0
6	24·1	75·9	71·9	28·1
7	28·9	71·1	71·7	28·3
8	31·8	68·2	71·6	28·4
9	32·2	67·8	72·0	28·0
10	34·8	65·2	72·0	28·0
11	36·1	63·9	72·2	27·8
12	42·0	58·0	72·2	27·8
13	46·2	53·8	72·2	27·8
14	58·7	41·3	74·2	25·8
15	60·8	39·2	80·5	19·5
16	59·6	40·4	85·6	14·4
17	60·9	39·1	91·7	8·3

Table III.

Temperature: 40·0.°

1	11·1	88·9	10·1	89·9
2	11·3	88·7	28·6	71·4
3	11·5	88·5	39·3	60·7
4	11·3	88·7	46·7	53·3
5	11·7	88·3	70·8	29·2
6	15·0	85·0	72·0	28·0
7	22·0	78·0	73·7	26·3
8	24·7	75·3	73·8	26·2
9	28·6	71·4	74·0	26·0
10	36·7	63·3	74·5	25·5
11	51·3	48·7	75·5	24·5
12	59·9	40·1	75·2	24·8
13	63·7	36·3	91·4	8·6

TABLE 4.

Temperature: 50·0°

No.	Sulphates in solution, in molar percentages. K_2SO_4	Na_2SO_4	Sulphates in residue, in molar percentages. K_2SO_4	Na_2SO_4
1	15·0	85·0	21·4	78·6
2	15·7	84·3	52·3	47·7
3	16·3	83·7	63·4	36·6
4	15·5	84·5	67·0	33·0
5	16·6	83·4	67·5	32·5
6	17·5	82·5	68·0	32·0
7	22·0	78·0	72·1	27·9
8	24·8	75·2	72·4	27·6
9	29·1	70·9	72·2	27·8
10	34·3	65·7	73·5	26·5

TABLE 5.

Temperature: 600°.

1	16·8	83·2	12·4	87·6
2	17·2	82·8	45·5	54·5
3	16·7	83·3	60·6	39·4
4	17·4	82·6	63·4	36·6
5	20·3	79·7	64·6	354
6	25·8	74·2	66·3	33·7
7	31·6	68·4	69·0	31·0
8	35·6	64·4	70·4	29·6
9	43·8	56·2	72·8	27·2
10	48·6	51·4	72·7	27·3
11	62·9	37·1	74·2	25·8
12	67·3	32·7	74·3	25·7
13	66·8	33·2	77·3	22·7
14	68·7	31·3	87·8	12·2

TABLE 6.

Temperature: 70·0°.

1	17·8	82·2	19·6	80·4
2	17·8	82·2	38·6	61·4

No.	Sulphates in solution, in molar percentages. K_2SO_4	Na_2SO_4	Sulphates in residue, in molar percentages. K_2SO_4	Na_2SO_4
3	17·4	82·6	47·3	52·7
4	18·0	82·0	56·2	43·8
5	17·8	82·2	68·4	31·6
6	17·3	82·7	68·9	31·1
7	18·3	81·7	69·3	30·7
8	19·1	80·9	69·3	30·7
9	23·3	77·7	70·8	29·2
10	28·6	71·4	72·3	27·7
11	34·5	65·5	73·1	26·9
12	34·7	65·3	73·2	26·8
13	55·3	44·7	75·2	24·8
14	68·9	31·1	75·8	24·2
15	69·4	30·6	82·6	17·4

TABLE 7.

Temperature: 80·0°.

1	19·2	80·8	16·3	83·7
2	19·7	80·3	46·8	53·2
3	19·2	80·8	51·0	49·0
4	19·8	80·2	59·5	40·5
5	20·1	79·9	68·5	31·5
6	20·0	80·0	70·1	29·9
7	24·2	75·8	72·0	28·0
8	25·3	74·7	71·6	28·4
9	30·6	69·4	74·1	25·9
10	38·3	61·7	74·9	25·1
11	51·2	48·8	75·2	24·8
12	64·2	35·8	74·9	25·1
13	70·4	29·4	87·4	12·6
14	70·7	29·3	93·0	7·0

These results are represented in square diagrams in Fig. 2 to 8. the horizontal side representing the composition of residue, and the vertical that of the salts in solution.

Fig. 2.

Temperature: 15·0°.

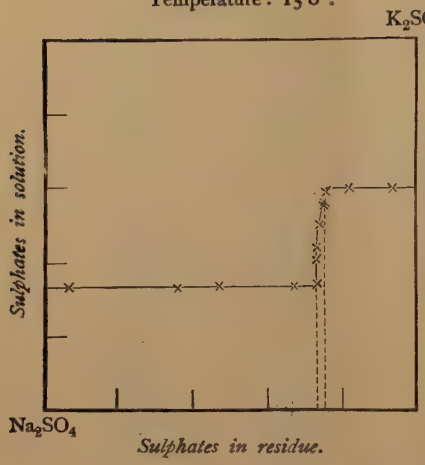


Fig. 3.

Temperature: 25·0°.

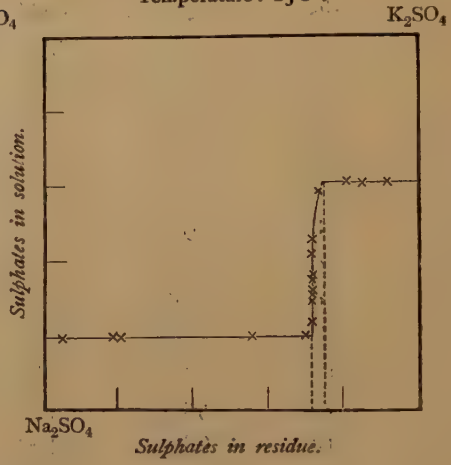


Fig. 4.

Temperature: 40.0°.

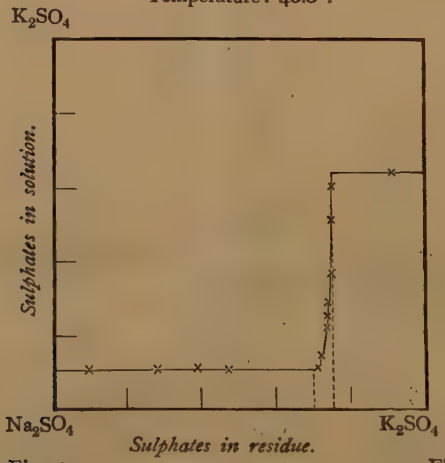


Fig. 5.

Temperature: 50·0°.

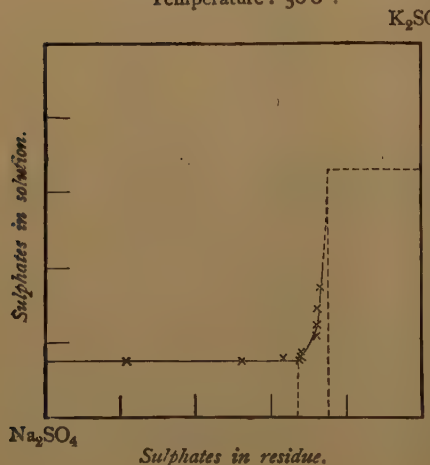


Fig. 6.

Temperature: 60·0°.

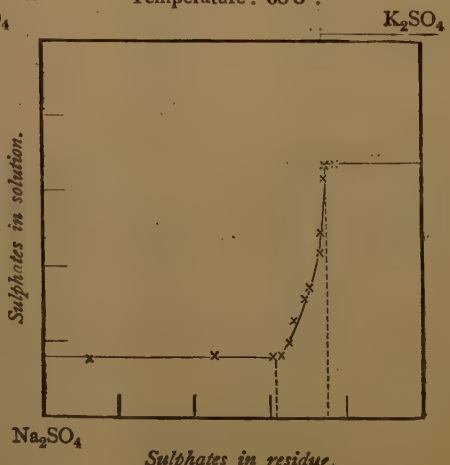


Fig. 7.

Temperature: 70·0°

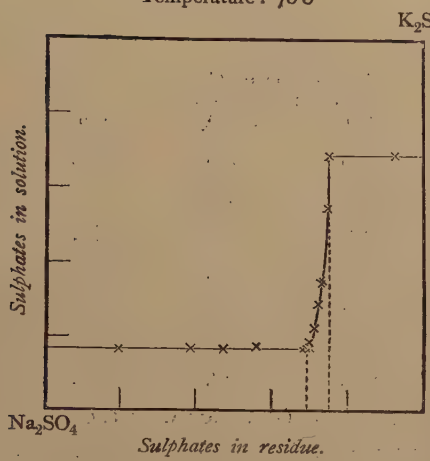
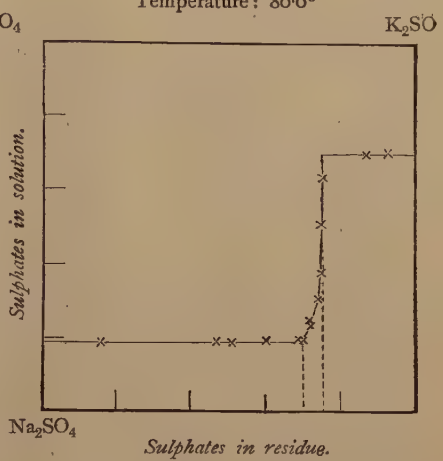


Fig. 8.

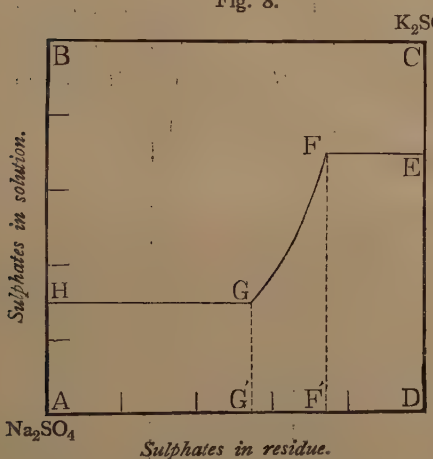
Temperature: 80·0°



Discussion.

The curves in these seven figures have a general form as shown in Fig. 9,[1] where

Fig. 8.



C represents a pure saturated solution of potassium sulphate;

CE solution saturated with potassium sulphate together with a gradually increasing quantity of soduim sulphate;

EF solutions saturated with potossium sulphate and a residue represented by the point *F'*;

FG a solution, as the residue, having a series of solid solutions of which the composition varies from *F'* to *G'*;

GH solutions saturated with sodium sulphate and a residue represented by the point *G'*;

HA solutions saturated with sodium sulphate, with a gradually decreasing quantity of potassium sulphate;

A a pure saturated solution of sodium sulphate.

Now it is clear from the figure that at least one of the point *F'*

1 The curve FG is concave to the residue axis at lower temperatures.

and G' must represent a double salt. The following table derived from Fig. 2 to 8 will decide.

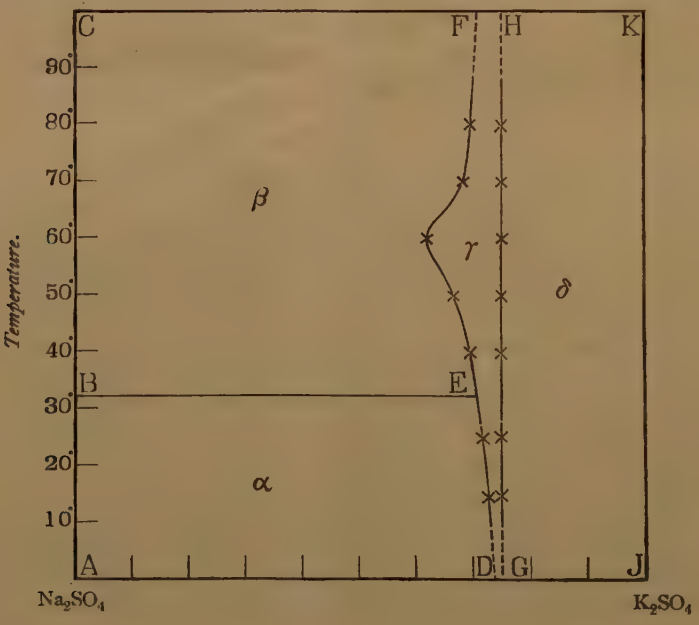
TABLE 8.

Temperature.	Composition of F', in molar percentages. K_2SO_4	Na_2SO_4	Composition of G', in molar percentages. K_2SO_4	Na_2SO_4	Difference.
15·0°	75·0	25·0	73·0	27·0	2·0
25·0°	75·0	25·0	71·7	28·3	3·3
40·0°	75·0	25·0	69·5	30·5	5·5
50·0°	(75·0)	(25·0)	66·7	33·3	(8·3)
60·0°	75·0	25·0	61·8	38·2	13·2
70·0°	75·0	25·0	68·8	31·2	6·2
80·0°	75·0	25·0	69·5	30·5	5·5

As seen from the table, the composition of G' varies with a change of temperature but that of F' does not; and it may be inferred that the residue represented by F' is a compound but the other not. The point F' just corresponds to the formula $K_3Na(SO_4)_2$, and the point G' represents the double salt saturated with sodium sulphate, and the curve GF has the double salt unsaturated with sodium sulphate as the residue.

To test the influence of temperature on the solubility of sodium sulphate in the double salt, the data in the fore-going table are graphically represented in Fig. 10. In the figure, B being the transition

Fig. 10.



temperature of sodium sulphate from decahydrate to anhydrous, namely 32·383°, *AB* represents the decahydrated sodium sulphate and *BC* the anhydrous. The curve *DEF* represents the double salt saturated with sodium sulphate, *GH* glaserite, and *JK* potasium sulphate. In the field α there exist decahydrated sodium sulphate and the double salt saturated with sodium sulphate, in β that solid solution and anhydrous sodium sulphate, in γ unsaturated solid solutions and in δ the double salt and potassium sulphate.

The results as a whole are concordant with those of Nacken as far as 60°; but above that temperature the field of the solid solution becomes narrower again, whereas Nacken assumed it to widen with the rise of temperature up to 180°.

Summary.

1. Sodium and potassium sulphates form a double salt of the formula $K_3Na(SO_4)_2$.

2. This double salt dissolves sodium sulphate as a solid solution but not potassium sulphate.

3. The limit of the solid solutions has been determined for the temperature interval from 15° to 80°.

In conclution I wish to express my sincere thanks to Prof. Y. Osaka for his valuable suggestions and kind instruction.

On the Beckmann Rearrangement. V.

Rearrangement of Diphenylketoxime Benzenesulphonyl Ester and Synthesis of Phenylbenzimido-benzenesulphonate.

By

Mitsuru Kuhara,
Kaoru Matsumiya and Naohiko Matsunami.

(Received November 30, 1914.)

As has already been mentioned in the previous articles[1] by one of us (M.K.) and his collaborators, diphenylketoxime benzenesulphonyl ester actually undergoes the spontaneous molecular rearrangement, whose primary cause may be ascribed to the dissociation of the benzenesulphonic acid residue of strongly negative character as we assume, with the consequent formation of phenylbenzimido-benzenesulphonate, thus giving a possible explanation as regards the mechanism of the Beckmann rearrangement.

Diphenylketoxime benzenesulphonyl ester used in the present work was prepared from the sodium salt of diphenylketoxime[2] by the action of benzenesulphonyl chloride[3] at the ordinary temperature. It is a colourless crystalline substance, whose nature was confirmed by saponification with alkali by which process it splits up readily into its constituents, i.e., diphenylketoxime and benzenesulphonic acid. As a matter of fact, the ester changes by the molecular rearrangement to a yellow viscid liquid, which is no doubt phenylbenzimido-benzenesulphonate, slowly on being allowed to stand by itself in a solid state in a chloroform solution, or by exposing its powder to the ultra-violet rays, but instantaneously with explosive violence accompanied by a hissing noise on heating above its melting point 62°; thus the change should be as follows, as has already been shown[4]:

---

1 Mem. Coll. Sci. Engin., Kyoto, **2**, 385 (1910); **4**, 1 (1913); these Memoirs, **1**, 52 (1914).

2 Ber. D. chem. Ges., **17**, 812 (1884).

3 Lieb. Ann., **87**, 299 (1853); Z. f. Chem., 1866, 106.

4 *Loc. cit.*

$$\begin{array}{c} C_6H_5.C.C_6H_5 \\ \| \\ N.OSO_2.C_6H_5 \end{array} \longrightarrow \begin{array}{c} C_6H_5.C.OSO_2.C_6H_5 \\ \| \\ N.C_6H_5 \end{array}$$

Colourless crystals. Yellow viscid liquid.

Diphenylketoxime benzenesulphonyl ester Phenylbenzimido-benzenesulphonate.

Phenylbenzimido-benzenesulphonate which is of unstable character, gradually changes to benzanilide and benzenesulphonic acid by moisture on being left in open air, but very readily by treating with water, sometimes still further decomposition taking place with the production of aniline, benzoic acid and benzenesulphonic acid, when is kept in a moist chloroform solution; thus the reactions should be as follows:

$$\begin{array}{c} C_6H_5.C.OSO_2.C_6H_5 \\ \| \\ N.C_6H_5 \end{array} \xrightarrow{\text{water}} \begin{array}{c} C_6H_5.CO \\ | \\ NH.C_6H_5 \end{array} + C_6H_5.SO_2.OH$$

$$\begin{array}{c} C_6H_5.C.OSO_2.C_6H_5 \\ \| \\ N.C_6H_5 \end{array} \xrightarrow{\text{water}} \begin{array}{c} C_6H_5.COOH + C_6H_5.SO_2.OH \\ \hline H_2N.C_6H_5 \end{array}$$

Phenylbenzimido-benzenesulphonate was then synthesized from phenylbenzimido-chloride[1] by the action of silver benzenesulphonate[2]. In this experiment, phenylbenzimido-chloride prepared as purely as possible with all necessary precautions, and dissolved in petroleum ether was allowed to react with silver benzenesulphonate under constant and vigorous shaking, and then the solid separated from petroleum ether by filtration was treated with chloroform. Evaporating chloroform by passing a rapid current of dry air through the solution, there was left a yellow viscid liquid, some benzanilide separated from the concentrated solution having been removed by filtration through cotton wool. The substance, thus prepared by synthesis corresponds to phenylbenzimido-benzenesulphonate, inferring its composition from the analytical results; hence the reactions should be represented as follows:

$$\begin{array}{c} C_6H_5.C.Cl \\ \| \\ N.C_6H_5 \end{array} + AgOSO_2.C_6H_5 \longrightarrow \begin{array}{c} C_6H_5.C.OSO_2.C_6H_5 \\ \| \\ N.C_6H_5 \end{array} + AgCl$$

The substance possesses the same behaviours as the benzenesulphonate formed by the rearrangement of diphenylketoxine benzenesulphonyl

1 Lieb. Ann., **184**, 79 (1877); Ber. D. chem. Ges., **43**, 892 (1910).

2 Lieb. Ann. **223**, 244 (1884).

ester, thus readily decomposing into benzanilide and benzenesulphonic acid, and also into benzoic acid, benzenesulphonic acid and aniline by the action of water.

Further, the absorption spectra of the two preparations of phenylbenzimido-benzenesulphonate from two different sources, that is, one formed by rearrangement and the other prepared by synthesis, were examined under the same condition. On comparing their absorption curves, as will be seen in the experimental part, it has been found that they almost agree to each other.

Now from the experimental results so far obtained a conclusion is drawn that phenylbenzimido-benzenesulphonate formed from diphenylketoxime benzenesulphonyl ester is identical with that obtained by synthesis from phenylbenzimido-chloride and silver benzenesulphonate. It is, therefore, quite evident that diphenylketoxime benzenesulphonyl ester undergoes the molecular rearrangement spontaneously, owing to the presence of the benzenesulphonic acid residue of strongly negative character without the aid of any reagent, more readily by the mere elevation of temperature; consequently the production of the acyl derivative of the substituted imido-acid from the ketoxime acyl ester must be a necessary condition of the Beckmann rearrangement.

EXPERIMENTAL PART.

1. *Sodium Salt of Diphenylketoxime*, $(C_6^1H_5)_2C{:}N.ONa$.

Since the method of the preparation of the sodium salt of diphenylketoxime proposed by Spiegler[1] gives a very poor yield, the authors have suggested the other method which is very simple and satisfactory. It consists in adding thin slices of metallic sodium to the solution of diphenylketoxime in absolute ether, by which treatment there was noticed a brisk evolution of hydrogen and the deposition of the sodium salt of diphenylketoxime in the form of a light white powder. The latter was then separated from the unchanged metallic sodium left in ether by decantation after shaking the whole mixture violently, and then repeatedly washed with ether until not a trace of diphenylketoxime unchanged is detected in washings. The salt thus prepared was dried in a desiccator and analysed.

1 Ber. D. chem. Ges., **17**, 812 (1884).

0·1594 grm. substance gave 0·08 grm. Na_2SO_4

	Calc. for $(C_6H_5)_2C{:}N.ONa$	Found
Sodium	10·47	10·56

As a by-product of the reaction there was found a small quantity of aminodiphenylmethane, $(C_6H_5)_2CH.NH_2$, whose formation is undoubtedly due to the reduction of diphenylketoxime by hydrogen liberated.

2. *Diphenylketoxime Benzenesulphonyl Ester,*

$(C_6H_5)_2C{:}N.OSO_2.C_6H_5$.

Equivalent quantities of the sodium salt of diphenylkotoxime and benzenesulphonyl chloride[1] mixed in absolute ether were allowed to react to each other for several hours under vigorous shaking. The etherial solution, then separated by filtration from sodium chloride formed in the reaction, was made to evaporate by passing a current of dry air in order to avoid the rise of temperature, by which process colourless crystals of diphenylketoxime benzenesulphonyl ester were deposited. Repeating its recrystallization from ether, it was obtained in pure state. The ester was analysed, and gave the following value for sulphur.

0·186 grm. substance gave 0·126 grm. $BaSO_4$.

	Calc. for $(C_6H_5)_2C{:}N.OSO_2.C_6H_5$.	Found
Sulphur	9·51	9·30

The substance is soluble in alcohol, benzene and chloroform, and melts at 62° with some change.

In order to confirm the nature of the ester, it was treated with alcoholic potash by the action of which it was found to decompose into diphenylketoxime and benzenesulphonic acid. The former was identified by its melting point and the latter by the analysis of its barium salt which gave the following value for barium.

0·109 grm. of the anhydrous salt gave 0·555 grm. $BaSO_4$.

	Calc. for $(C_6H_5.SO_2O)_2Ba$	Found
Barium	30·42	30·13

[1] Lieb. Ann., **87**, 299 (1853).

3. *Phenylbenzimido-benzenesulphonate,*

$C_6H_5.C.(OSO_2.C_6H_5):N.C_6H_5$

By heating the crystals of diphenylketoxime-benzenesulphonyl ester above its melting point, they change instantaneously to a yellow viscid liquid with an explosive violence accompanied by a hissing sound. Such a change is, however, gradually effected on allowing the crystals to stand under a desiccator for a long while, or by dissolving them in chloroform, the solution getting slowly yellow, It was also observed that the ester in the form of fine powder, when introduced between a pair of thin quartz plates and exposed to the ultra-violet rays from a mercury lamp, changes yellow on its surface in an hour. The analysis of the substance gave the following values for sulphur.

I. 0·1140 grm. substance gave 0·0762 grm. $BaSO_4$,
II. 0·1552 „ „ „ 0·1214 „ „
III. 0·1062 „ „ „ 0·0741 „ „

	Calc. for	Found			
	$C_6H_5.C.(OSO_2.C_6H_5):N.C_6H_5$	I	II	III	Mean
Sulphur	9·51	9·17	10·07	9·30	9·52

The yellow viscid liquid is without doubt phenylbenzimido-benzenesulphonate formed by the molecular rearrangement of diphenylketoxime benzenesulphonyl ester, as it readily decomposes into benzanilide and benzenesulphonic acid by treating with water. Benzanilide was confirmed by its melting point and other properties, and benzenesulphonic acid by the analysis of its barium salt.

0·2 grm. of the anhydrous barium salt gave 0·108 grm. $BaSO_4$.

	Calc. for $(C_6H_5.SO_2O)_2Ba$	Found
Barium	30·42	31·79

The substance, when exposed to air, slowly decomposes into benzanilide and benzenesulphonic acid owing to its unstable nature in presence of moisture; it is, however, pretty stable in vacuum. It is soluble in alcohol, chloroform and acetone. By keeping its solution in moist chloroform for a while, some colourless silky needle-shaped crystals were found to separate out. They melt above 200° with decomposition, and soluble in water, alcohol and acetone. They decompose into aniline and benzenesulphonic acid by treating with a solution of alkali;

aniline isolated by extracting with ether was confirmed by its colour-reaction with a bleaching powder solution, and benzenesulphonic acid contained in the alkaline aqueous part by the analysis of its barium salt.

0·115 grm. of the anhydrous barium salt gave 0·0598 grm. $BaSO_4$.

	Calc. for $(C_6H_5.SO_2O)_2Ba$	Found
Barium	30·42	30·60

The mother liquor consisting of the chloroform solution was evaporated, and from the residue benzoic acid was isolated and confirmed by its melting point and other characteristic properties. The substance which consists of silky needles is, therefore, the aniline salt of benzenesulphonic acid ; and on comparing it with the salt prepared according to Gericke[1] from aniline and benzenesulphonic acid, both were found to be identical. Hence phenylbenzimido-benzenesulphonate in the chloroform solution decomposes, in fact, into aniline benzenesulphonic acid and benzoic acid through the action of moisture contained in it.

4. Synthesis of Phenylbenzimido-benzenesulphonate.

Phenylbenzimido-benzenesulphonate was synthesized from phenylbenzimido-chloride and silver benzenesulphonate, and the process will be described below. Phenylbenzimido-chloride (benzanilidimide chloride) was prepared according to the method proposed by Wallach[2] and purified by the process suggested by Mumm[3] with all possible precautions, and the anhyduous silver benzenesulphonate was obtained by Hübner's method.[4] Phenylbenzimido-chloride, thus prepared, was dissolved in dry petroleum ether, and anhydrous silver benzenesulphonate added in some excess over an equivalent quantity. With the constant and vigorous shaking of the mixture, silver benzenesulphonate gradually changed yellow on its surface, and finally a yellow substance deposited in the wall of a vessel. After removing petroleum ether by decantation, the yellow substance was extracted by treating the residue with chloroform which produced a deeply yellow-coloured solution. Evaporating chloroform by passing a current af dry air through the chloroform solution

1 Lieb. Ann., **100**, 217 (1857).
2 Ibid., **184**, 79 (1877).
3 Ber. D. chem. Ges., **43**, 892 (1910).
4 Lieb. Ann., **223**, 244 (1884).

well excluded from moisture, there was left a yellow viscid liquid, mixed with some colourless crystals. The liquid was then separated from the crystals by filtering through cotton wool with the aid of a suction pump. The crystals were identified as benzanilide by its melting point and all other properties. In order to remove the trace of chloroform admixed in the viscid liquid, the latter was left in a desiccator for several hours under constant exhaustion, until no evolution of the bubbles of chloroform was noticed. The substance was analysed and gave the following values for sulphur.

I. 0·5749 grm. substance gave 0·3835 grm. $BaSO_4$

II. 0·6092 ,, ,, ,, 0·4522 ,, ,,

	Calc. for $C_6H_5.C.(OSO_2.C_6H_5):N.C_6H_5$	Found I	Found II	Found Mean
Sulphur	9·51	9·19	10·22	9·71

The substance is soluble in alcohol, chloroform and acetone, but difficultly in ether and petroleum ether. By adding water to its solution in acetone, there was found to separate out a flocky precipitate which, when recrystallized from alcohol, melted at 161°, thus proving to be benzanilide. From the filtrate benzenesulphonic acid was isolated as its barium salt by adding some baryta water and removing the excess of barium by means of carbon dioxide. The barium salt recrystallized from water was analysed.

0·425 grm. of the salt gave 02·13 grm. $BaSO_4$

	Calc. for $Ba(C_6H_5SO_2O)_2{}^1/_2H_2O$	Found
Barium	29·83	29·49

The substance dissolved in moist chloroform was also noticed to deposit some colourless silky crystals of the aniline salt of benzenesulphonic acid whose formation must be due to the decomposition of phenylbenzimido-benzenesulphonate into aniline, benzoic acid and benzenesulphonic acid through the action of moisture contained in chloroform, since by treating the crystals with aqueous alkali they yield aniline and benzenesulphonic acid. The former was confirmed by its colour reaction with a bleaching powder solution and the latter by the production of its barium salt.

0·2381 grm. of the crystals gave 0·2306 grm. $BaSO_4$ by analysis.

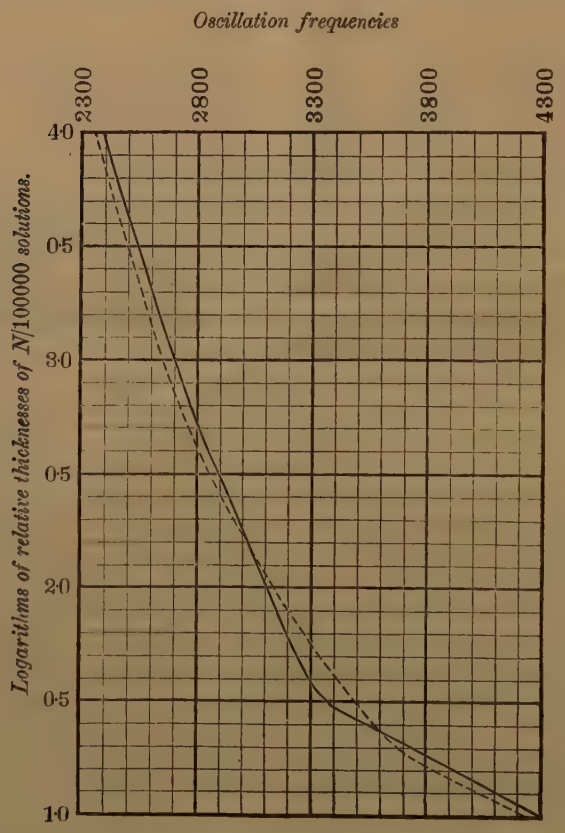
	Calc. for $C_6H_5.SO_2O.NH_3.C_6H_5$	Found
Sulphur	12·78	13·30

Aniline benzenesulphonate, thus formed, is identical with that prepared according to Gericke's method.[1]

As has been shown so far, phenylbenzimido-benzenesulphonate prepared by synthesis shows no difference in all of its properties in comparison with that formed by the molecular rearrangement of diphenylketoxime benzenesulphonyl ester, hence they should be identical.

5. *Absorption Spectra of the two Preparations of Phenylbenzimido-benzenesulphonate.*

For the further confirmation of identity of the two preparations of phenylbenzimido-benzenesulphonate, spectrographic experiments were



[1] *Loc cit.*

conducted according to the well known method by Hartley.[1] For this purpose, their solutions were prepared in absolute alcohol and a Hilger quartz spectrograph was employed with an iron arc as the source of light. An observation was repeated in each case for the different thicknesses of the liquids of several different dilutions with the use of Baly's adjustable cell,[2] and the absorption curves were plotted with the oscillation frequencies and the relative thicknesses of liquids in terms of the dilution of N/100000. On comparing the curves showing the absorption spectra of the two preparations from the different sources, as represented in the figure, they almost agree to each other, so that they may be concluded to be identical. Thus the full line curve represents the absorption spectra of phenylbenzimido-benzenesulphonate formed by the rearrangement of diphenylketoxine benzenesulphonyl ester and the dash line curve that of the same substance prepared by synthesis from phenylbenzimido-chloride and silver benzenesulphonate.

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[1] J. chem. Soc., **47**, 685 (1885).

[2] Ibid., **85**, 1039 (1904).

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CONTENTS.

PAGE.

On the Systems: Barium Oxide—Acetic Acid—Water and Maginesium Oxide—Acetic Acid—Water.

By Junichi Iwaki. - - - - - - - - - - - 81

A New Method for the Determination of Sodium and Potassium in a Mixture of their Salts.

By Kichirō Okada. - - - - - - - - - - - 89

On the Double Salt of Sodium and Potassium Sulphates.

By Kichirō Okada. - - - - - - - - - - - 95

On the Beckmann Rearrangement. V. Rearrangement of Diphenylketoxime Benzenesulphonyl Ester and Synthesis of phenylbenzimido-benzenesulphonate.

By Mitsuru Kuhara, Kaoru Matsumiya and Naohiko Matsunami. - 105